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MATHEMATIK

Bemerkungen über die Methoden von Trefftz und Ritz

von

K. MAURIN

Vorgelegt von S. MAZUR am 7. September 1955

In dieser Note werden die Verfahren von Trefftz und Ritz verallgemeinert und ihr Zusammenhang mit der Methode der orthogonalen Projektion gezeigt.

1. Definitionen. Ω_n ist ein beschränkter Bereich des n-dimensionalen Raumes. $x=(x_1,\dots,x_n)\in\Omega_n$; $A=\sum\limits_{|p|\leqslant 2m} a_p(x)D^p$, wo $p=(p_1,\dots,p_n)$ ein Differentiationsindex, $|p|=p_1+\dots+p_n$ $D^p=D_x^p=\dfrac{\partial^{|p|}}{\partial x_{11}^p\dots\partial x_n^{pn}}$ ist. A ist formal selbstadjungiert, d. h.

$$Af(x)=\sum_{|p|\leqslant 2m} a_p(x)D^pf(x)=\sum_{|p|\leqslant 2m}(-1)^{|p|}D^p(\overline{a_p(x)}f(x));$$

$a_p\in C^{2m+|p|}(\Omega_n)$ und ist beschränkt in Ω_n.

$L^2(\Omega_n)$ ist der Hilbertsche Raum mit dem Skalarprodukt

$$(f,g)=\int_{\Omega_n} f(x)\overline{g(x)}\,dx;\quad \|f\|=(f,f)^{1/2}.$$

Es sei $\partial^p=\dfrac{\partial^{|p|}}{\partial x_1^{p_1}\dots\partial x_n^{p_n}}$ ein Differentialoperator; sein Definitionsgebiet $C_0^\infty(\Omega_n)$ ist die Menge der beliebig oft in Ω_n differenzierbaren Funktionen mit kompakten Trägern in Ω_n. Der Operator $(-1)^p(\partial^{|p|})^*$ heisst der Operator der schwachen (verallgemeinerten) Differentiation, wobei im Sinne des Hilbertschen Raumes $L^2(\Omega_n)$ der Operator $(\partial^p)^*$ der zu ∂^p adjungierte Operator ist. Wir werden ihn im folgenden auch mit D^p bezeichnen.

D^p ist bekanntlich schwach (also auch stark) abgeschlossen (vgl. [1]).

2. Der Raum $H(A)$ und seine orthogonale Zerlegung. Von dem Operator A und dem Bereich Ω_n wird vorausgesetzt, es gäbe ein solches qua-

dratisches Funktional (im allgemeinen werden es mehrere sein)

$$(f,f)_A \overset{\mathrm{df}}{=} \int_{\Omega_n} \Big\{ \sum_{|\alpha|=|\beta|=m} a_{\alpha\beta}(x) D^\alpha f(x) \overline{D^\beta f(x)} + \dots \overset{\text{Ableitungen der Ordnung} < m}{\Big\}} dx,\ f \in C^{2m}(\Omega_n),$$

dass:

1^0 $Af(x)=0$ die Euler-Lagrange Gleichung des Funktionals $(f,f)_A$ ist,

2^0 $(f,f)_A \geqq c \int_{\Omega_n} \sum_{|p|\leqq m} |D^p f(x)|^2 dx$, wo $c>0$ eine von f unabhängige positive Konstante bedeutet*). Wenn wir jetzt in $C^{2m}(\Omega_n)$ das Skalarprodukt

3^0 $(f,g)_A \overset{\mathrm{df}}{=} \int_{\Omega_n} \Big\{ \sum_{|\alpha|=|\beta|=m} a_{\alpha\beta}(x) D^\alpha f(x) \overline{D^\beta g(x)} + \dots \Big\} dx$ einführen und diesen prähilbertschen Raum vervollständigen, bekommen wir den Hilbertschen Raum $H(A)$. Wie aus 2^0 folgt (vgl [1]), haben die Elemente von $H(A)$ alle schwachen Ableitungen bis zur Ordnung m. Die Norm des Elementes

$$h \in H(A): \|h\|_A = \Big[\int_{\Omega_n} \Big\{ \sum_{|\alpha|=|\beta|=m} a_{\alpha\beta}(x) D^\alpha h(x) \overline{D^\beta h(x)} + \dots \Big\} dx \Big]^{1/2},$$

wo D^α jetzt schwache Ableitungen bedeuten.

$Z(A) \subset H(A)$ ist die Abschliessung (in der $\| \ \|_A$-Metrik) der Menge $C_0^{2m}(\Omega_n)$; $z \in Z(A)$ bedeutet bekanntlich, dass z und alle seine Ableitungen jeder Ordnung $<m$ am Rande von Ω_n verschwinden (vgl. [1], [7], [8]).

Das orthogonale Komplement von $Z(A)$: $H(A) \ominus Z(A)$ wird $U(A)$ genannt. Wir haben also die orthogonale Zerlegung

$$H(A) = U(A) \oplus Z(A). \tag{2.1}$$

Es gilt das folgende

LEMMA: *Wenn $u \in U(A)$, dann ist $Au=0$; genauer: u ist nach der Korrektur auf einer Nullmenge gleich einer $2m$-mal stetig differenzierbaren in Ω_n Lösung der Gleichung $Au=0$.*

Die Lösung des Dirichletschen Problems: "Gesucht ist die Lösung u der Gleichung $Au=0$ ($u \in C^{2m}(\Omega_n)$, die am Rande dieselben Werte, wie $f \in H(A)$ annimmt, d. h. $(u-f) \in Z(A)$" wird erhalten durch die Orthogonalprojektion P von f auf $V(A)$: $u=Pf$.

Beweis: wegen (2.1) haben wir $(u,z)_A=0$ identisch für $z \in Z(A)$, also auch (wegen 1^0 und 3^0) $0=(u,\varphi)_A=(u,A\varphi)$ identisch für $\varphi \in C_0^{2m}(\Omega_n)$. u ist also eine schwache Lösung der elliptischen Gleichung mit regulären Koeffizienten $Au=0$. Nach einem Ergebnis des Verfassers [6] ist also u (nach der Korrektur auf einer Nullmenge) eine klassische Lösung von $Au=0$; $u \in C^{2m}(\Omega_n)$ w. z. b. w.

Dieselbe Schlussweise erlaubt einen analogen Satz für formalselbstadjungierte elliptische Gleichungssysteme auszusprechen. Unser Ergebnis

*) Diese Bereiche heissen im Falle $A=\sum_{i=1}^{n} \frac{\partial^2}{\partial x_i^2}$ Gebiete von Soboleff [8].

ist eine Verallgemeinerung eines gleichlautenden Satzes von M. Kodaira [4], (der Fall einer einzigen Gleichung zweiter Ordnung) und stimmt mit einem Ergebnis von Višik [6] überein.

3. Zwei Näherungsverfahren. Es sei $v_1, v_2, \ldots$ eine Basis von $U(A)$, $v_l \in C^{2m}(\Omega_n)$ $l=1,2,\ldots$ U_k – der auf $v_1,\ldots,v_k$ aufgespannte Raum; P_k – die orthogonale Projektion auf U_k. Es gilt der folgende

SATZ 1. 1° *Die Folge $P_k f$, $k=1,2,\ldots$, konvergiert in der $\| \ \|_A$ – Norm gegen die klassische (also nicht nur gegen eine verallgemeinerte) Lösung des Dirichletschen Problems*;

2° $\|P_k f\|_A \leqslant \|P_{k+1} f\|_A \leqslant \|u\|_A$;

3° *die k-te Näherung* $P_k f = u_k = \sum_{i=1}^{k} c_i v_i$, *wo die Koeffizienten* c_i, $i=1,2,\ldots,k$, *den verallgemeinerten Trefftzschen Gleichungen*

$$\sum_{i=1}^{k} c_i (v_i, v_l)_A = (f, v_l)_A, \qquad l=1,2,\ldots,k \tag{3.1}$$

genügen.

4° *In jeder kompakten Untermenge von Ω_n konvergiert die Folge (u_k) mit allen Ableitungen (bis zur Ordnung $2m$) gegen u gleichmässig.*

Beweis: ad 1° und 2°: die Behauptung folgt aus dem Lemma und der Definition von P_k; ad 3°: da $(f-P_k f, v_l)_A = 0$ $l=1,2,\ldots,k$), ist (3.1) bewiesen; ad 4°: da $u_k = P_k f$ eine Lösung der Gleichung $Au_k = 0$ ist, existiert (nach einem, von dem Verfasser bewiesenen Satze [6]) zu jedem $\mathring{x} \in \Omega_n$ eine solche Umgebung $V(\mathring{x}) \ni \mathring{x}$, dass

$$u_k(x) = \int_{V(\mathring{x})} r(x,y)\, u_k(y)\, dy \quad \text{identisch für} \quad x \in V(\mathring{x}), \tag{3.2}$$

wobei $r(x,y) \in C^{2m}(\overline{V(\mathring{x})} \times \overline{V(\mathring{x})})$.

Nach der Differentiation der beiden Seiten von (3.2) haben wir wegen der Schwarzschen Ungleichung:

$$|D^p u_k(x) - D^p u_{k+l}(x)| = \int_{V(\mathring{x})} D_x^p r(x,y)[u_k(y) - u_{k+l}(y)]\, dy| \leqslant$$

$$\leqslant K(p, V(\mathring{x}))\, \|u_k - u_{k+l}\| \underset{k\to\infty}{\to} 0,$$

wo

$$K(p, V(\mathring{x})) = \Big[\max_{x \in \overline{V}(\mathring{x})} \int_{V(\mathring{x})} |D_x^p r(x,y)|^2\, dy\Big]^{1/2}, \quad |p| \leqslant 2m.$$

Nach dem Borel-Lebesgueschen Satze folgt daraus die Behauptung.

Bemerkung: Im Falle eines glatten $\partial\Omega_n$ (des Randes von Ω_n) können wir die Gleichung (3.1) folgendermassen umformen:

$$\sum_{i=1}^{k} c_i (v_i, v_l)_A = \sum_{i=1}^{k} \int_{\partial\Omega_n} c_i B(v_i, v_l)(x)\, dx = \int_{\partial\Omega_n} B(f, v_l)(x)\, dx \quad l=1,2,\ldots,k, \tag{3.1'}$$

wo $B(,)$ die bilineare Form in der Greenschen Formel bedeutet.

(3.1) sind also die verallgemeinerten Trefftzschen Gleichungen [2], [3]. Unser Satz gibt also zugleich eine geometrische Interpretation des Treffzschen Verfahrens.

4. Eine Bemerkung über die Methode von Ritz. Es sei $z_1, z_2, \ldots$ eine Basis von $Z(A)$; Z_k der auf $z_1, z_2, \ldots, z_k$ aufgespannte Raum; Π bzw. Π_k die orthogonale Projektion auf $Z(A)$ bzw. $Z_k(A)$. Die Lösung des Dirichletschen Problems kann man natürlich auch auf folgende Weise erhalten(vgl. (2.1)):

$$u = f - \Pi f.$$

Es liegt jetzt das folgende Verfahren nahe:

SATZ 2. *Es sei*

$$u_k \overset{\mathrm{df}}{=} f - \Pi_k f \qquad k = 1, 2, \ldots$$

Dann konvergiert die Folge (u_k) *(in der* $\| \ \|_A$*-Metrik) gegen die klassische Lösung* u *des Dirichletschen Problems.* $\Pi_k f = \sum_{i=1}^{k} b_i z_i$, *wobei die Koeffizienten* b_i *aus den Ritzschen Gleichungen*

$$\sum_{l=1}^{k} b_i (z_i, z_l)_A = (f, z_l)_A \qquad l = 1, 2, \ldots, k$$

bestimmt werden. Für die Ritzschen Näherungen gelten die Umgleichungen:

$$\|u_k\|_A \geqslant \|u_{k+l}\|_A \geqslant \|u\|_A \qquad k = 1, 2, \ldots$$

Der Beweis dafür ist klar.

5. Gemischte Probleme können auf dieselbe Weise behandelt werden; man muss bloss statt $H(A) = V(A) \oplus Z(A)$ die von Višik angegebene orthogonale Zerlegung des von ihm eingeführten Raumes anwenden [6]. Man bekommt dann auch nach dem Vorbild der §§ 3, 4 die "Trefftzsche" und "Ritzsche" Folge.

Es gelten dann auch analoge Sätze.

6. Die Übertragung aller obigen Ergebnisse auf formal selbstadjungierte Gleichungssysteme erhält man durch die Interpretation von u, f, u_i, v_l u. s. w. als Vektorfelder $u = (u^1(x), \ldots, u^r(x))$ u. s. w. mit Werten aus einem r-dimensionalen unitären Raume.

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MATHEMATICS

Remark on the Factorization of Spaces

by

P. J. HILTON (Cambridge, England)

Presented by K. BORSUK on September 30, 1955

If the space X is homeomorphic to the topological product $Y \times Z$, K. Borsuk has described the spaces Y and Z as *factors* of X and has raised the question of the extent to which a space determines its prime factors. Contribution to this question have been made by Borsuk, Whitehead, Fox, and Kosiński [1] — [5]. In particular Borsuk has established some conditions under which factorization is unique and Whitehead and Fox have produced (non-trivial) examples where it is not. Fox also raises the question whether the homotopy type of Z is determined by X and Y when X is suitably restricted.

Our object in this note is to draw attention to an obvious consequence of the assumption that X has finitely-generated homology groups and also to a second consequence that follows from a theorem due to Serre [6].

THEOREM. *Suppose X is a connected space of the homotopy type of $Y \times Z$, and that the singular homology groups of X are finitely-generated in each dimension. Then the singular homology groups of X and Y determine those of Z.*

If, moreover, X is simply-connected, then the homotopy groups of X and Y determine those of Z.

We first prove a lemma.

LEMMA. *If G is a finitely-generated Abelian group and if $G \cong A+B$, then G and A determine B (up to isomorphism).*

Proof. Since G is finitely-generated and since there exist homomorphisms of G onto A, B, it follows that A, B are finitely-generated. As subgroups of an isomorphic image of G they are Abelian. A finitely-generated Abelian group is determined (up to isomorphism) by its rank and prime-power invariants. Clearly the rank of B is the excess of the rank of G over that of A. Also the prime-power invariants of $A+B$ are just those of A together with those of B. It follows that the prime-power

invariants of B are precisely the residue when the prime-power invariants of A are removed from those of G.

Thus the rank and prime-power invariants of B are determined and the lemma is proved.

Reverting to the theorem, we invoke the Künneth formula for the singular homology groups of a topological product, which we write in the invariant form *),

$$H_n(Y\times Z)\cong\sum_{p+q=n}H_p(Y)\otimes H_q(Z)+\sum_{p+q=n-1}H_p(Y)*H_q(Z).$$

Now X has the homotopy type of $Y\times Z$ and the singular homology groups are invariant of homotopy type. Thus

$$H_n(X)\cong\sum_{p+q=n}H_p(Y)\otimes H_q(Z)+\sum_{p+q=n-1}H_p(Y)*H_q(Z),\quad\text{all}\quad n\geqslant 0.$$

We now argue, by induction with respect to n, that $H_n(Z)$ is determined by the homology groups of X and Y in dimensions $\leqslant n$. This is certainly true, if $n=0$, since the connectedness of X implies that $H_0(Y)$ and $H_0(Z)$ are cyclic infinite. Suppose then that the above statement about $H_n(Z)$ is true if $n<k$. We have

$$\begin{aligned}H_k(X)&\cong\sum_{\substack{p+q=k\\p>0}}H_p(Y)\otimes H_q(Z)+\sum_{p+q=k-1}H_p(Y)*H_q(Z)+H_k(Z)\\&=A\qquad\qquad\qquad\qquad\qquad\qquad+B,\ \text{say.}\end{aligned}$$

By the inductive hypothesis, A is determined by the homology groups of X and Y in dimensions $\leqslant k$, so that, by the lemma, B, or $H_k(Z)$, is also determined by the homology groups of X and Y in dimensions $\leqslant k$. The induction is established and the first part of the theorem proved. We remark that to show that the homology groups of Y and Z are finitely-generated it is unnecessary to use the Künneth formula; it is sufficient to observe that the projections $Y\times Z\to Y$, $Y\times Z\to Z$ induce homomorphisms of the homology groups of $Y\times Z$ on to those of Y, Z.

The second part of the theorem follows from the result, due to Serre, that if a simply-connected space has finitely-generated singular homology groups, then it also has finitely-generated homotopy groups. We have only to use the isomorphisms

$$\pi_n(X)\cong\pi_n(Y\times Z)\cong\pi_n(Y)+\pi_n(Z)$$

and apply the lemma.

*) Given two additive Abelian groups A, B, the *tensor product* $A\otimes B$ is defined as the group generated by all pairs (a,b), $a\in A$, $b\in B$, subject to the relations $(a+a',b)=(a,b)+(a',b)$, $(a,b+b')=(a,b)+(a,b')$, $a,a'\in A$, $b,b'\in B$.

Let A be represented as F/R, where F is free Abelian. Then it may be shown that the kernel of the injection $R\otimes B\to F\otimes B$ is determined (up to isomorphism) by A and B. This kernel, written $A*B$, is called the *torsion product* of A and B.

If X is not simply-connected then Serre's theorem cannot be applied *); nor does the lemma apply to the consideration of the fundamental group of Z. To consider the deeper question whether the homotopy types of X and Y determine that of Z, it should be possible to investigate the Postnikov invariants of Z; the Postnikov invariants of $Y \times Z$ are given by the formula

$$k^n(Y \times Z) = k^n(Y) + k^n(Z)$$

with certain obvious identifications.

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*) For example if $X = S^2 \vee S^1$, a 2-sphere and circle with a single common point, then $\pi_2(X)$ is free Abelian on $\aleph_0$ generators. However, it is generated by a single element as a $\pi_1(X)$-module.

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MATHEMATICS

On Some Properties of Mappings of the Sphere into the Euclidean Space

by

J. W. JAWOROWSKI

Presented by K. BORSUK on October 5, 1955

1. Let S_n be the n-dimensional sphere, in the $(n+1)$-dimensional Euclidean space E_{n+1}, i. e., the set of points $x \in E_{n+1}$ with $|x|=1$. We denote by a the antipodal mapping of S_n. It is defined by $a(x)=-x$. A set $E \subset S_n$ is called *antipodal*, if $a(E)=E$.

A compact space M is said to be *p-acyclic*, if every $(r-1)$-dimensional true cycle modulo 2 of M (in the sense of Vietoris), with $0 \leqslant r \leqslant p$, is homologous to zero in M (see [5], p. 247, 248). Thus, for instance, M is 0-acyclic if, and only if, it is not empty; M is 1-acyclic if, and only if, it is a continuum; the sphere S_n is n-acyclic but not $(n+1)$-acyclic.

We shall prove the following

THEOREM I. *Let F be a closed antipodal subset of S_n, containing a closed antipodal $(n-1)$-acyclic subset K. Then there exists a real-valued continuous function f defined in S_n such that F is the set of all points $x \in S_n$ for which*

$$f(x)=fa(x). \tag{1}$$

Moreover, f is constant on F.

This theorem is an extension of Theorem 2 of [4] on the case of spheres of arbitrary dimension. The proof of Theorem 2 in [4] is based on a lemma which results directly from a theorem of S. Eilenberg (see [3], théorème 4, p. 269). We prove Theorem I of the present paper in an analogous way, by using the following generalization of Eilenberg's theorem mentioned above which is proved in [5]:

(*) *A closed $(n-1)$-acyclic subset of S_n disconnects S_n between every antipodal pair of points belonging to its complement* (see [5], p. 249).

Proof of Theorem I. By (*), K disconnects S_n between every antipodal pair of points of its complement. Let $R_1, R_2, \ldots$ be a sequence (finite or infinite) of components of $S_n - F$. Since F is antipodal and

since $K \subset F$, then, for every $x \in S_n - F$, the points x and $a(x)$ belong to different components of $S_n - F$. Hence none of the components $R_1, R_2, \ldots$ is antipodal and, for every k, it is $a(R_k) = R_{j_k}$, where $j_k \neq k$. Therefore, one may enumerate the components of $S_n - F$ such that $a(R_1) = R_2$, $a(R_3) = R_4 \ldots$ Putting $G = R_1 + R_3 + R_5 + \ldots$ we have $S_n - F = G + a(G)$. As in [4] we set

$$f(x) = \begin{cases} \varrho(x, F) & \text{for} \quad x \in G + F \\ -\varrho(x, F) & \text{for} \quad x \in a(G) + F. \end{cases}$$

Thus f is a function which satisfies the conditions of Theorem I.

2. Let f be a continuous mapping of S_n into E_n and let F be the set of points $x \in S_n$ which satisfy the condition (1). Then F is antipodal and, by Borsuk's theorem on antipodes (see [1], p. 178, Satz II), $F \neq 0$.

We shall prove the following

THEOREM II. *Let F be an arbitrary non-empty closed antipodal subset of S_n. Then there exists a continuous mapping f of S_n into E_n such that F is the set of all points $x \in S_n$ which satisfy the condition* (1). *Moreover, f is constant on F.*

Proof. Let $x_0 \in F$ and let P be the n-dimensional hyperplane in E_{n+1} passing through the origin and perpendicular to the diameter $\overline{x_0, a(x_0)}$ of S_n. Let p be the projection of S_n into P, paralell to $\overline{x_0, a(x_0)}$. We set

$$f(x) = \varrho(x, F) \cdot p(x)$$

(in the sense of multiplication of points by scalars). Since $p(-x) = -p(x)$ for every $x \in S_n$, the mapping f satisfies the conditions of Theorem II.

3. Theorem 1 of [4] and a generalization of Borsuk's theorem on antipodes given in [2] suggest the following:

PROBLEM. *Let F be a closed antipodal subset of S , containing a closed p-acyclic subset K. Does there exist a continuous mapping f of S_n into E_{n-p} such that F is the set of all points $x \in S_n$ which satisfy the condition* (1)?

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MATHÉMATIQUE

Une propriété de dualité équivalente à celle de Janiszewski

par

A. LELEK

Présenté par K. KURATOWSKI le 6 Octobre 1955

Entendons par X *le continu localement connexe* (c'est-à-dire une image biunivoque et bicontinue du segment de droite) dans un espace métrique compact. D'après un théorème de K. Kuratowski ([2], p. 374), la propriété suivante, dite de Janiszewski ([2], p. 353), caractérise topologiquement la surface de sphère parmi les X qu'aucun point ne coupe:

(J) *C_1 et C_2 étant des continus situés dans X et dont la partie commune C_1C_2 n'est pas connexe, leur complément $X-(C_1+C_2)$ ne l'est non plus.*

R. Kapała a établi récemment dans son travail de licence (d'ailleurs pour d'autres buts et par voie différente) la dualité suivante, supposée il y a plusieurs années par K. Zarankiewicz pour cette surface:

(Z) *C et R étant respectivement un continu et une région, situés dans X et dont les compléments $X-C$ et $X-R$ sont connexes, la connexité de $C-R$ entraîne celle de $R-C$ et réciproquement.*

Je vais démontrer le théorème suggéré à ce propos par B. Knaster, à savoir que, pour X, il y a l'équivalence entre (Z) et (J).

LEMME. (Z) *entraîne l'unicohérence de X* *).

Démonstration. Soit R une région dont

(1) le complément $X-R$ est connexe.

L'espace étant un continu localement connexe, la propriété (1) entraîne l'existence de la décomposition suivante de R ([2], p. 189, 2):

$$R=\sum_{i=1}^{\infty} H_i \quad \text{où} \quad H_i, \text{ sont des continus,} \tag{2}$$

$$H_i \subset \operatorname{Int}(H_{i+1}), \tag{3}$$

*) C'est-à-dire la connexité de la partie commune de deux continus arbitraires dont la somme constitue X.

(4) $X-H_i$ sont connexes

pour $i=1,2,\ldots$ On a $H_i\overline{R-H_{i+1}}\subset \mathrm{Int}(H_{i+1})\overline{X-H_{i+1}}=0$ d'après (3), donc $(\sum_{i=1}^{\infty}H_i)\prod_{i=1}^{\infty}\overline{R-H_i}=0$, c'est-à-dire $R\prod_{i=1}^{\infty}\overline{R-H_i}=0$ d'après (2), ce qui entraîne en vertu de l'inclusion triviale $\prod_{i=1}^{\infty}\overline{R-H_i}\subset\overline{R}$ que

$$\prod_{i=1}^{\infty}\overline{R-H_i}\subset\overline{R}-R.$$

Réciproquement, en tenant compte de (2), on a $\overline{R}-H_i=\overline{R}-\overline{H_i}\subset R-H_i$ pour $i=1,2,\ldots$, d'où

$$\overline{R}-R=\overline{R}-\sum_{i=1}^{\infty}H_i=\prod_{i=1}^{\infty}(\overline{R}-H_i)\subset\prod_{i=1}^{\infty}\overline{R}-H_i.$$

On a donc

$$\prod_{i=1}^{\infty}\overline{R-H_i}=\overline{R}-R=\mathrm{Fr}(R). \tag{5}$$

Tout H_i-R étant connexe, comme vide d'après (2), on conclut de (1) et (4) en vertu de la propriété (Z) appliquée à R et à $C=H_i$ que $\overline{R-H_i}$ est connexe, donc que $\overline{R-H_i}$ est un continu pour $i=1,2,\ldots$ Vu (3), il en est de même de $\prod_{i=1}^{\infty}\overline{R-H_i}$, c'est-à-dire de $\mathrm{Fr}(R)$ d'après (5). Or, la connexité de cette frontière équivaut à l'unicohérence de l'espace ([1], p. 148-150), c. q. f. d.

THÉORÈME. (Z) *équivaut à* (J).

Démonstration. (Z) entraîne (J). Trois cas sont à distinguer:

1° Les ensembles $X-C_1$ et $X-C_2$ sont connexes. En posant $X-C_2=R$, il vient

$$C_1C_2=C_1(X-R)=C_1-R \quad \text{et}$$
$$X-(C_1+C_2)=(X-C_1)(X-C_2)=(X-C_1)R=R-C_1.$$

En appliquant (Z) à C_1 et R, on en conclut donc que si C_1C_2 n'est pas connexe, $X-(C_1+C_2)$ ne l'est non plus, c'est-à-dire que l'on a (J).

2° Au moins un des ensembles $X-C_1$ et $X-C_2$ n'est pas connexe et chacun d'eux n'a que tout au plus une seule composante qui empiète sur l'autre. Si elles existent, désignons-les par R_1 et R_2 respectivement; sinon, posons de même $R_1=0$ ou $R_2=0$. On a donc par définition

$$(X-C_1)-R_1=(X-C_1)(X-R_1)\subset C_2 \quad \text{et} \tag{6}$$
$$(X-C_2)-R_2=(X-C_2)(X-R_2)\subset C_1,$$

d'où

$$[(X-C_1)(X-R_1)]\,[(X-C_2)(X-R_2)]=0. \tag{7}$$

Les ensembles

$$K_1=C_1+(X-C_1)(X-R_1)=X-R_1 \quad \text{et} \quad K_2=C_2+(X-C_2)(X-R_2)=X-R_2 \tag{8}$$

sont des continus ([2], p. 88, 5). On a d'une part

$$X=(C_1+R_1)+(C_2+R_2) \tag{9}$$

en vertu de (7), les deux sommandes en parenthèses étant des continus; en effet, C_1 et R_1 sont connexes par définition; ils ne sont pas séparés, car — comme on sait ([2], p. 169, 3) — $\mathrm{Fr}(R_1)\subset\mathrm{Fr}(C_1)\subset C_1$ et $\overline{C_1+R_1}=C_1+R_1+\mathrm{Fr}(R_1)\subset C_1+R_1$; il en est de même de C_2+R_2. En appliquant (Z) à la décomposition (9), on en conclut donc en vertu du lemme que $(C_1+R_1)(C_2+R_2)$ est un continu.

D'autre part, en tenant compte de (6) et (7), on a

$$K_1K_2=C_1C_2+(X-C_1)(X-R_1)+(X-C_2)(X-R_2)=C_1C_2+[X-(C_1+R_1)(C_2+R_2)], \tag{10}$$

d'où la décomposition $X=K_1K_2+(C_1+R_1)(C_2+R_2)$. On en conclut en vertu du même lemme que la connexité de K_1K_2 entraînerait celle de l'ensemble $K_1K_2(C_1+R_1)(C_2+R_2)$, donc celle de l'ensemble C_1C_2, avec lequel il coïncide en vertu de (10), et de l'inclusion triviale

$$C_1C_2\subset(C_1+R_1)(C_2+R_2).$$

En admettant donc les hypothèses de (J), K_1K_2 n'est pas connexe et, en vertu de (8), $X-K_1$ et $X-K_2$ sont connexes. Il s'ensuit d'après 1°, en y substituant K_1 à C_1 et K_2 à C_2, que l'ensemble $X-(K_1+K_2)$ n'est pas connexe. Or,

$$X-(K_1+K_2)=X-[C_1+(X-C_1)(X-R_1)+C_2+(X-C_2)(X-R_2)]=(X-C_1)(C_1+R_1)(X-C_2)(C_2+R_2)=X-(C_1+C_2),$$

la première égalité résultant de (8) et la dernière — des formules

$$X-C_1\subset C_2+R_2 \quad \text{et} \quad X-C_2\subset C_1+R_1,$$

équivalentes à (6). Ainsi, $X-(C_1+C_2)$ n'est pas connexe; on a donc la thèse de (J).

3° Au moins deux composantes A et B de $X-C_1$ empiètent sur $X-C_2$. Alors les sous-ensembles non-vides $A-C_2$ et $B-C_2$ de l'ensemble $X-(C_1+C_2)$ se trouvent situés dans ses composantes distinctes, puisqu'elles le sont dans les composantes distinctes A et B de son sur-ensemble $X-C_1$. Ainsi, $X-(C_1+C_2)$ a au moins deux composantes; on a donc encore (J).

(J) entraîne (Z). Posons $C_1=C$ et $C_2=X-R$. Par conséquent $X-(C_1+C_2)=X-[C+(X-R)]=(X-C)R=R-C$ et $C_1C_2=C(X-R)=C-R$. En admettant donc, conformément aux hypothèses de (Z), que C et $X-R$ sont des continus, il résulte de (J) que la connexité de $R-C$ entraîne celle de $C-R$.

Réciproquement, posons $R_1=R$ et $R_2=X-C$. Par conséquent $X-(R_1+R_2)=C-R$ et $R_1R_2=R-C$. En admettant donc, conformément aux hypothèses de (Z), que R et $X-C$ sont des régions, on conclut d'un énoncé équivalent à (J) (voir [2], p. 355, 5) que la connexité de $C-R$ entraîne celle de $R-C$. Ainsi, les deux parties de la thèse de (Z) sont réalisées.

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MATHÉMATIQUE

Une définition de distribution

par
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Présenté par S. MAZUR le 15 Octobre 1955

On connait, à présent, plusieurs définitions des *distributions* dites aussi *fonctions généralisées*. La première, due à S. Soboleff [1], envisage les distributions comme des fonctionnelles linéaires, définies sur certains espaces de fonctions. La même définition a été employée par L. Schwartz [2]. J. Mikusiński [3] a donné une définition équivalente sans faire appel à la notion de fonctionnelle, en obtenant les distributions comme la fermeture de l'espace de fonctions continues, pourvu d'une notion convenable de convergence faible. Cette définition a aussi servi à G. Temple [4] dans ses recherches sur des fonctions généralisées. Enfin, I. Halperin [5], H. König [6] et R. Sikorski [7] ont donné des définitions, où les distributions sont considérées comme des dérivées formelles des fonctions continues ou bien intégrables.

Le but de cette note est de donner une définition de distribution qui présente certains avantages par rapport aux définitions précédentes. Cette définition est très simple et a paru utile dans des applications, par exemple, dans les processus stochastiques. L'idée essentielle est la même que dans le travail de Mikusiński cité ci-dessus, mais la notion de convergence faible sera plus naturelle et mieux adaptée à des applications pratiques.

Une suite de fonctions $f_n(x)$, continues dans l'intervalle $-\infty < x < \infty$, est dite *fondamentale* lorsqu'il existe une suite de fonctions $F_n(x)$ et un entier $k \geqslant 0$ tels que

(a) $F_n^{(k)}(x) = f_n(x)$ ($F_n^{(k)}$ la dérivée d'ordre k de F_n);

(b) $F_n(x)$ converge presque uniformément (c'est-à-dire uniformément sur tout compact).

Deux suites fondamentales $f_n(x)$ et $g_n(x)$ sont dites *équivalentes* lorsqu'il existe deux suites $F_n(x)$ et $G_n(x)$ et un entier $k \geqslant 0$ tels que

(a) $F_n^{(k)}(x) = f_n(x)$ et $G_n^{(k)}(x) = g_n(x)$;

(β) $F_n(x)$ et $G_n(x)$ convergent presque uniformément vers la même limite.

Les distributions sont, par définition, des classes de suites fondamentales équivalentes.

Il est très utile, et même important dans certaines applications, de désigner les distributions par des symboles $f(x)$, $g(x)$, etc., comme les fonctions, dont elles sont une généralisation. Alors la variable x n'aura plus qu'un sens symbolique, pareillement, à peu près, que dans la théorie des fonctions mesurables.

Toute distribution $f(x)$ peut évidemment être représentée par une suite fondamentale quelconque $f_n(x)$, appartenant à la classe considérée; on écrira $f(x)=[f_n(x)]$.

Par la somme $f(x)+g(x)$ de deux distributions $f(x)=[f_n(x)]$ et $g(x)=[g_n(x)]$ on entend la distribution $[f_n(x)+g_n(x)]$. Pareillement on définit le produit $af(x)$ et la translation $f(x+h)$, où a et h sont des nombres.

Toute distribution $f(x)$ peut être représentée par une suite fondamentale $w_n(x)$ dont tous les termes sont des polynômes: $f(x)=[w_n(x)]$.

Par la $m^{\text{ème}}$ dérivée d'une distribution $[w_n(x)]$, où $w_n(x)$ sont des polynômes, on entend la distribution $[w_n^{(m)}(x)]$. Ainsi toute distribution est évidemment dérivable. De plus, toute distribution est une dérivée (d'ordre $k\geqslant 0$) d'une fonction continue.

On dit qu'une suite de distributions $f_n(x)$ converge vers une distribution $f(x)$ lorsqu'il existe un entier $k\geqslant 0$ et des fonctions continues $F_n(x)$ et $F(x)$, telles que $F_n(x)$ converge presque uniformément vers $F(x)$ et que l'on a $F_n^{(k)}(x)=f_n(x)$, $F^{(k)}(x)=f(x)$. Pareillement on définit la convergence d'une famille de distributions $f_a(x)$ avec un paramètre a continu. Pour toute distribution $f(x)$ on a

$$\lim_{a\to 0}\frac{f(x+a)-f(x)}{a}=f'(x).$$

Toute suite convergente de distributions peut être dérivée terme à terme.

L'avantage de la théorie précédente est qu'elle est tout à fait élémentaire et facile et que toutes les démonstrations sont presque triviales. De plus, il faut remarquer que cette théorie ne fournit que les ainsi dites *distributions d'ordre fini*, c'est-à-dire celles qui sont les plus importantes dans les applications et qui constituent la plus étroite généralisation des fonctions telle que toute fonction généralisée (distribution) soit dérivable et que toute suite convergente soit dérivable terme à terme. Le passage à des généralisations plus larges, en particulier à des distributions d'ordre infini, ne présente d'ailleurs aucune difficulté. On peut aussi construire une théorie analogue pour le cas de pulsieurs variables.

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ASTROPHYSICS

Polarization of the Solar Corona During the Total Solar Eclipse of June 30, 1954

by
A. G. PACHOLCZYK

Presented by A. SOŁTAN on September 8, 1955

The author made photographic measurements of the polarization of the solar corona during the total solar eclipse of June 30-th, 1954. The photographs were taken in the village of Sejny in the Suwałki district. The camera was a Zeiss, the focal length of the lens was 11 cms. and its luminosity ratio 1:4.5. The film used was Agfa Isopan. A polaroid filter was placed in front of the lens, it was revolved with the lens of the camera. The author obtained three exposures of the corona in three vibration planes of the polaroid filter, each separated by 60°. The measurements of the negatives were made along the equatorial and polar lines. The degree of polarization is defined as

$$P=\frac{i_1-i_2}{i_1+i_2}, \tag{1}$$

where i_1 is the light intensity in a definite vibration plane at a given point of the corona, i_2 is the light intensity in a plane perpendicular to the first one at the same point. The degree of polarization is calculated from the formula

$$P=\frac{2\sqrt{a(a-b)+b(b-c)+c(c-a)}}{a+b+c}, \tag{2}$$

where a, b, and c are the intensities at a definite point in the images obtained respectively for the three position angles of the vibration planes, separated by 60°. The values a, b, and c are interconnected by the system of equations [1] resulting from Malus's law

$$\begin{aligned} a&=i_1\cos^2\alpha+i_2\sin^2\alpha,\\ b&=i_1\cos^2(120^0-\alpha)+i_2\sin^2(120^0-\alpha),\\ c&=i_1\cos^2(60^0-\alpha)+i_2\sin^2(60^0-\alpha),. \end{aligned} \tag{3}$$

The scattering of light within the optical system of the camera and also the halo from the film were found to be negligible after the former research. The fog on the negative, caused by light diffusion in the earth's atmosphere and the process of developing is illustrated by a curve obtained by interpolation as shown in Fig. 1.

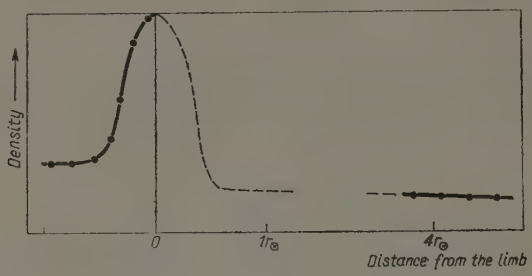

Fig. 1

The degree of polarization for various distances from the solar limb have been computed and the results are presented in Table I.

Table I

Distance from solar limb	Polarization degree (equator)	Maximum error (per cent)	Polarization degree (pole)	Maximum error (per cent)
0.6 $r_\odot$	0.30	8	—	—
0.8	0.48	7	0.30	8
1.0	0.40	6	0.28	18
1.2	0.45	5	0.28	37
1.4	0.46	5	0.27	45
1.6	0.35	7	—	—
1.8	0.40	9	—	—
2.0	0.37	11	—	—
2.2	0.30	15	—	—
2.4	0.38	21	—	—
2.6	0.35	28	—	—
2.8	0.25	46	—	—
3.0	0.19	58	—	—

From the results of the measurements the following conclusions may be drawn:

1. The degree of polarization of the solar corona is greater along the equatorial than along the polar line.

2. Along the equatorial line polarization is greatest at a distance of approximately one solar degree from the solar limb.

3. The curve representing the relation between the degree of polarization along the equatorial line and the distance from the solar limb (Fig. 2) corresponds, to the curve obtained by Vashakidse [2], at a dis-

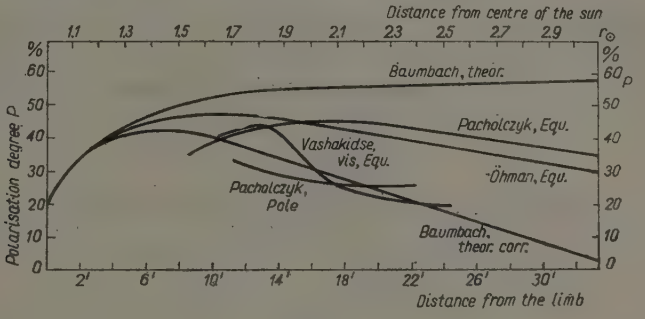

Fig. 2

tance of 11′-13′ from the solar limb, while the curve for the outer corona approximates in shape to Öhman's curve [4].

4. Accepting the values obtained by Grotrian [5] for the intensities J_F, J_K of the F and K components of the corona on the equator, and assuming that

$$(J_F+J_K)P=J_FP_F+J_KP_K \tag{4}$$

and that

$$P_F=\varkappa P_K, \tag{5}$$

where P_F and P_K are the degrees of polarization of the corresponding components of the corona and $\varkappa$ is the coefficient, it is possible to calculate the degree of polarization of the electronic component of the corona

$$P_K=\frac{P\left(1+\frac{J_F}{J_K}\right)}{1+\varkappa\frac{J_F}{J_K}}. \tag{6}$$

The values of P_K, when $\varkappa=0$ and $\varkappa=0.4$, are given in the third and fourth columns of Table II. When $\varkappa=0$, the values obtained for the degree of polarization of the K component of the corona are high. For the values assumed here for the ratio $J_F:J_K$, the degree of polarization — at great distances from the solar limb — nearest to the theoretical value of 0.63 was obtained when $\varkappa=0.4$. This value of $\varkappa$ is somewhat greater than that obtained by Öhman working on the same assumptions.

5. Assuming that for the same distance from the solar limb the degree of polarization of the various components of the corona on the

equator and at the pole is the same, it may be stated on the basis of equation (4) that

$$\left(\frac{J_F}{J_K}\right)_{\text{Pole}} = \frac{P_{\text{Eq}} - P_{\text{Pole}} + \{P_{\text{Eq}} - P_F\}\left(\frac{J_F}{J_K}\right)_{\text{Eq}}}{P_{\text{Pole}} - P_F}. \tag{7}$$

The values of the ratio $J_F:J_K$ along the polar line for both values of $\varkappa$, as obtained from equation (7), are tabulated in columns 5 and 6 of Table II. In these calculations the values of the ratio $J_F:J_K$ on the equatorial line were the same as those obtained by Grotrian.

Table II

Distance from solar limb	$J_F:J_K$ after Grotrian (equator)	P_K for equator		$J_F:J_K$ for pole	
		$\varkappa=0$	$\varkappa=0.4$	$\varkappa=0$	$\varkappa=0.4$
$0.6\,r_\odot$	0.35	0.40	0.35	—	—
0.9	0.64	0.72	0.58	1.48	3.50
1.2	1.05	0.92	0.64	2.28	4.11

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EXPERIMENTAL PHYSICS

Electron Diffraction Investigation of Semiconductive PbTe Layers

by

A. FELTYNOWSKI, I. GLASS and L. GRELEWICZ

Presented by A. SOŁTAN on September 4, 1955

The present paper is concerned with vacuum evaporated photosensitive PbTe layers [1].

These layers are usually prepared in a glass envelope with appropriate electrodes. The process, in principle, is one of twofold evaporation: in the first stage, the substance is evaporated onto a wall without electrodes, whence, in the second stage, it is made to evaporate onto the opposite wall bearing electrodes; the wall on which the PbTe vapour condenses is subjected to intense cooling. In order to prepare specimens for electron diffraction investigation, the envelope was opened after the first evaporation and a thin glass plate (cover-glass) was placed on the wall bearing the electrodes. This plate had grids of phosphor bronze covered and attached to it by a thin formvar film. The envelope was then closed and evacuated and the layer evaporated onto the wall bearing the glass plate with the grids. The photocell thus prepared, its photoconductive properties were investigated. It should be noted that the glass plate with the grids covered only part of the wall; on the remaining part, electrodes had been painted with "aquadag" and provided with tungsten leads. The photocell was then opened and the grid with PbTe layer adhering to the film was carefully deposited onto a specimen holder.

A diffraction pattern obtained by the authors employing electrons accelerated by 61 kV is presented in Fig. 1. X-ray investigation shows that PbTe forms crystals of NaCl type cubic structure [2]. The electron diffraction pattern, as seen from the table containing the diameters of the rings, does not correspond to cubic structure. A similar diffraction pattern was obtained with a PbTe layer evaporated onto the film directly from a tungsten stripe. Lead telluride powder used for making the layers was investigated with X-rays *) and found to have a NaCl type struc-

*) The authors are indebted to Mr. J. Krylov, who made these measurements.

ture, with the lattice constant equal to 6.36 Å. On the other hand, the system of rings in the electron diffraction pattern obtained with a thin layer (apart from faint rings 3 and 4, probably resulting from contaminations) corresponds to simple cubic structure of lattice constant 3.33 Å. Such inconsistency in the case of thin layers prepared by evaporation is an indication that a new form of PbTe is present. A possible explanation should be found in random distribution of the tellurium and lead atoms over the lattice points in the thin layer, resulting in extinction of those rings of the NaCl type structure, the intensity of which is determined by the difference in atom factors. Thus, a crystal lattice of the kind proposed shows an electron diffraction pattern corresponding to simple cubic structure with lattice constant halved.

Of the three analogous compounds PbS, PbSe, and PbTe, the properties of PbS are the best known. Experimental data and theoretical analysis [3] prove this compound to be only slightly ionic in character. The lesser difference in atomic numbers of the components in PbTe should cause the ionic properties to recede still further. These considerations should make the authors' assumption of the Pb and Te atoms replacing each other in the crystal lattice points seem more plausible.

The PbTe layers were also examined with the electron microscope; when magnified 10,000 times, they appeared to be homogeneous. Following illumination with an intense electronic beam for 10—20 seconds, the layer underwent changes: small crystals formed, at first very minute in size, and later on separate, scantily distributed crystals attaining 1000 Å (Fig. 2). Further illumination caused gaps in the layer (see Fig. 3).

The authors wish to express their gratitude to Professor L. Sosnowski for his valuable discussions in interpreting the results.

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TABLE

No.	D mm.	Intensity	Lattice indices $h\ k\ l$	$A=\frac{D}{\sqrt{h^2+k^2+l^2}}$
1	9.35	very strong	1 0 0	9.35
2	13.25	very strong	1 1 0	9.37
3	14.45	very faint		
4	15.55	very faint		
5	16.2	strong	1 1 1	9.35
6	18.65	strong	2 0 0	9.325
7	20.85	very strong	2 1 0	9.325
8	22.85	strong	2 1 1	9.325
9	26.35	medium	2 2 0	9.325
10	27.95	strong	{2 2 1} {3 0 0}	9.32
11	29.55	strong	3 1 0	9.35
12	30.9	strong	3 1 1	9.315
13	32.4	very faint	2 2 2	9.35
14	33.55	strong	3 2 0	9.31
15	34.75	strong	3 2 1	9.29
16	37.4	very faint	4 0 0	9.345
17	38.45	strong	{3 2 2} {4 1 0}	9.33
18	39.55	medium	3 3 0	9.32
19	40.6	faint	3 3 1	9.32
20	41.65	faint	4 2 0	9.31
21	42.7	faint	4 2 1	9.32
22	43.7	very faint	3 3 2	9.32
23	45.85	very faint	4 2 2	9.37
24	46.65	medium	{4 3 0} {5 0 0}	9.33
25	47.65	medium	{4 3 1} {5 1 0}	9.345
26	48.4	very faint	{3 3 3} {5 1 1}	9.32
27	50.25	medium	{4 3 2} {5 2 0}	9.33
28	51.05	very faint	5 2 1	9.32
29	52.8	very faint	4 4 0	9.33
30	53.7	very faint	{4 4 1} {5 2 2}	9.34
31	54.6	very faint	{4 3 3} {5 3 0}	9.37
32	59.9	very faint	{4 4 3} {5 4 0} {6 2 1}	9.35

Fig. 1. Diffraction pattern of PbTe layer

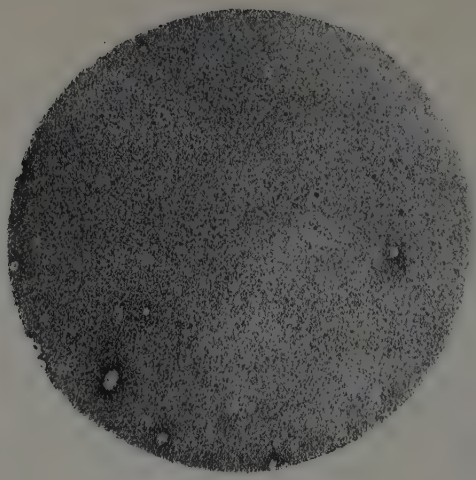

Fig. 2. Magnification 6.000 ×

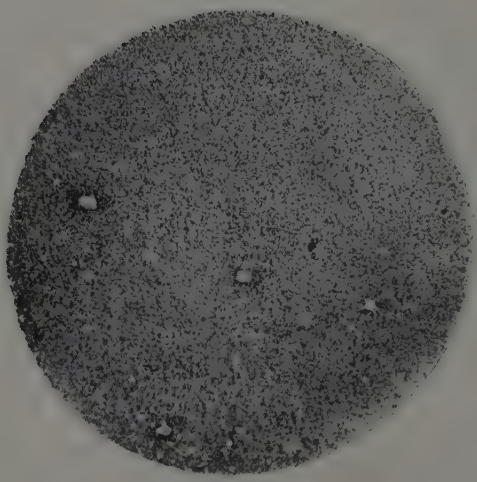

Fig. 3. Magnification 6.800 ×

Electron micrographs of PbTe layer exposed to intense electron beam

BULLETIN DE L'ACADÉMIE
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Series of Binary Positive Azeotropes

by

W. MALESIŃSKI

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of November 28, 1955

Introduction

The purpose of this paper is to analyse some of the consequences of Świętoslawski's scheme [1], [2], [3] in which agent A forms binary azeotropes (AH_i) with a series (H) of homologues and their isomers. This analysis is based on the assumption that the series of azeotropes form regular solutions [4], [5], [6]. The equations for regular solutions will be treated as semi-empirical.

The homologues H_k and H_e, forming tangent boiling temperature isobars [3] with the azeotropic agent A, determine the value called azeotropic range $Z_A(H)$ which is defined by the following equation (Fig. 1):

$$(1) \qquad Z_A(H)=T_{H_k}-T_{H_e}.$$

The symbol $Z_A(H)$ will be replaced below by Z. Its upper and lower portions are defined as follows:

$$(2) \quad Z_g=T_{H_k}-T_A, \quad Z_d=T_{A_k}-T_{H_e}.$$

The problem consists in relating value Z with the compositions and the boiling temperatures of the series of azeotropes as well as with the boiling temperature differences characterising agent A and the

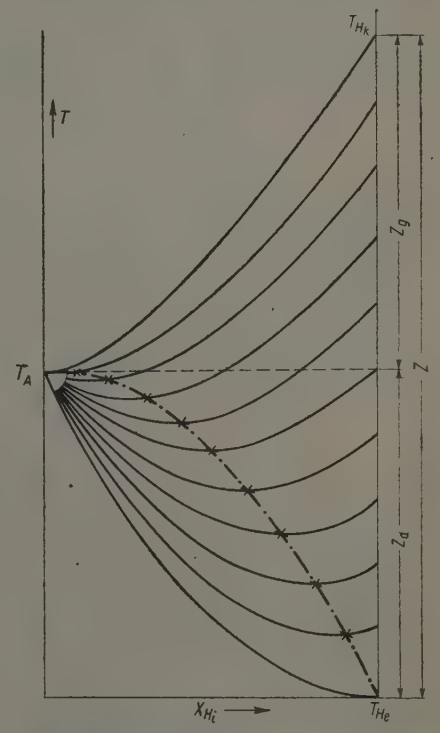

Fig. 1. A series of binary azeotropes formed by the azeotropic agent A with representatives of a series (H) of homologues and their isomers

representatives of a series (H) of homologues, their isomers and physicochemically closely related substances. The same problem has been investigated by Lecat [7] and Skolnik [8] but in a different manner. Prigogine [9] applied the regular solution theory to this problem. The differences arose from the fact that no definition was introduced for the azeotropic ranges and no general conclusions were made on the parameters resulting from a knowledge of the boiling temperature limits for the formation of the azeotropes by agent A and a series of homologues and their isomers.

Binary azeotropes have also been studied as regular solutions, especially their isotherms, by a number of other authors [9], [10].

General assumptions and basic relations

In this very short presentation only some general assumptions are given as well as the results obtained. We base our argument on the fundamental thermodynamic relations, valid for the azeotropic point under the assumption that the gaseous phases, being at equilibrium with the liquid phase, behave as ideal gases. This means that:

$$\begin{aligned} p_A^0(T_{Az}) f_A(T_{Az}, x_{H_i}) &= P, \\ p_{H_i}^0(T_{Az}) f_{H_i}(T_{Az}, x_A) &= P. \end{aligned} \tag{3}$$

where p_A^0 and $p_{H_i}^0$ are the vapour pressures of pure components, f_A and f_{H_i} represent activity coefficients for the azeotropic mixture, T_{Az} is the boiling temperature of the azeotrope under pressure P, x_A and x_{H_i} — mole fractions of components H_i in the azeotropic mixtures.

The activity coefficients are determined:

$$\begin{aligned} RT_{Az} \ln f_A &= A_{AH} x_H^2; \\ RT_{Az} \ln f_{W_i} &= A_{AH} x_A^2. \end{aligned} \tag{4}$$

According to our assumption the constant A_{AH} depends neither upon the temperature, nor upon representative H_i of the series (H), forming azeotropes of the (AH_i) type.

The vapour pressure of the given component, i, is determined by the well-known formula:

$$\ln p_i^0(T_{Az}) = \ln p + \int_{T_i}^{T_{A_z}} \frac{\Delta H_i}{RT^2} dT, \tag{5}$$

where T_i stands for the boiling temperature of the pure component under pressure P and ΔH_i is the latent heat of evaporation.

Combining equations (4) and (5) and at the same time taking into consideration equation (3) we obtain a system of equations:

$$(6)\qquad \begin{aligned} &\int_{T_A}^{T_{A_z}} \frac{\Delta H_A}{RT^2} dT + \frac{A_{AH}}{RT_{Az}} x_{H_i}^2 = 0, \\ &\int_{T_{H_i}}^{T_{Az}} \frac{\Delta H_{H_i}}{RT^2} dT + \frac{A_{AH}}{RT_{Az}} x_A^2 = 0. \end{aligned}$$

Relations between azeotropic parameters

We assume that the evaporation enthalpy does not change its value with temperature changes. If so, the following equation resulting from (6) may be written:

$$(7)\qquad \begin{aligned} \delta_A &= \frac{A_{AH}}{\Delta S_A} x_H^2, \\ \delta_{H_i} &= \frac{A_{AH}}{\Delta S_{H_i}} x_A^2 \end{aligned}$$

where the values $\delta_A = T_A - T_{A_z}$ and $\delta_{H_i} = T_{H_i} - T_{A_z}$ represent the azeotropic depressions with respect to agent A and homologue H_i respectively; ΔS_A and ΔS_{H_i} correspond to the evaporation entropy of A and H_i at boiling temperatures.

If the assumption is made that the evaporation entropy in the homologous series (H) is constant and if the conditions for tangent azeotropes remain fulfilled ($x_A = 1$, $\delta_A = 0$ or $x_{H_e} = 1$, $\delta_{H_e} = 0$), the following conclusion is correct

$$(8)\qquad \begin{aligned} \delta_A &= Z_d x_H^2, \\ \delta_{H_i} &= Z_g x_A^2. \end{aligned}$$

Therefore Z_d and Z_g are equal to

$$(9)\qquad Z_d = \frac{A_{AH}}{\Delta S_A}, \qquad Z_d = \frac{A_{AH}}{\Delta S_H}$$

and the evaporation entropy, ΔS_H, is constant for all of the homologues of series (H). If we assume that the entropy of evaporation of agent A is equal to that of the H homologues, it follows from equation (9) that the upper portion of the azeotropic range is equal to the lower one:

$$(10)\qquad Z_d = Z_g.$$

Then equations (8) become as follows:

$$\delta_A = \tfrac{1}{2} Z x_{H_i}^2, \qquad \delta_{H_i} = \tfrac{1}{2} Z x_A^2. \tag{11}$$

If we accept simplification (10), further relations valid for a series of binary azeotropes may be obtained on the basis of equations (11).

The azeotropic composition is determined by the two equations,

$$x_{H_i} = \frac{1}{2} + \frac{\Delta_A}{Z}, \qquad x_A = \frac{1}{2} + \frac{\Delta_{H_i}}{Z}, \tag{12}$$

where $\Delta_A = T_A - T_{H_i}$ and $\Delta_{H_i} = T_{H_i} - T_A$ are equal to the temperature differences of the components forming the respective azeotropes of series (H) with agent A.

The azeotropic depressions and boiling temperature differences are related to one another in the following way:

$$\Delta_A = -\tfrac{1}{2} Z + \sqrt{2Z}\,\sqrt{\delta_A}, \qquad \Delta_{H_i} = -\tfrac{1}{2} Z + \sqrt{2Z}\,\sqrt{\delta_{H_i}}. \tag{13}$$

Equations (13) are similar to those of Prigogine, being deduced from the same assumptions. They differ only in form. In our case it is shown that Δ_A and Δ_{H_i} are linear functions of $\sqrt{\delta_A}$ and $\sqrt{\delta_{H_i}}$.

I wish to express my thanks to Professor W. Świętosławski for his help and assistance.

Summary

On the basis of the definition given by Świętosławski for the azeotropic range Z of agent A with respect to a series (H) of homologues, their isomers and closely related substances, the following relations have been derived:

$$\delta_A = Z_d x_H^2$$

$$x_A = \frac{1}{2} + \frac{\Delta_{Hi}}{Z}$$

$$\Delta_A = -\frac{1}{2} Z + \sqrt{2Z}\,\sqrt{\delta_A},$$

where $\Delta_A = T_A - T_{H_i}$; $\delta_A = T_A - T_{Az}$ and $\Delta_{H_i} = T_{H_i} - T_A$ (T_A and T_{H_i} – boiling temperatures of pure components, T_{Az} – boiling temperature of binary azeotropic mixture), x_A and x_{H_i} mole fractions of components of azeotropic mixture.

The same equations are correct for the values of $\Delta_{H_i} = T_{H_i} - T_A$, x_{H_i} and $\delta_{H_i} = T_{H_i} - T_{Az}$.

These relations were derived from the equation for regular solutions:

$$RT \ln f_A = A_{AH} x_{H_i}^2$$

$$RT \ln f_{H_i} = A_{AH} x_A^2$$

and assuming that A_{AH} is constant for the whole series of AH_i azeotropes.

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CHEMISTRY

The Crossing Isobars Method for Determining the Composition and the Boiling Temperature of Saddle Azeotropes. XXII

by

W. ŚWIĘTOSŁAWSKI and W. TRĄBCZYŃSKI

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of November 28, 1955

Introductory remarks

The peculiar character of the tridimensional, boiling temperature isobars of ternary positive-negative azeotropes has led one of us to describe a method for examining the composition and the boiling temperature of these azeotropes [1]. It has been called the method of "horizontal isobars". In the present paper the description of another method is given, whereby it is possible to combine both the fractional distillation and the ebulliometric method so as to exploit the advantages offered by each of them. The very flat shape of the tridimensional boiling temperature isobars makes it somewhat difficult to obtain by fractional distillation a main fraction F, corresponding to the real composition of the ternary saddle azeotrope. In spite of this, fraction F, is usually almost entirely free of impurities, because most of them are collected in the forerunnings and in the bottom product. As to the ebulliometric method, it enables us to prove whether fraction F, corresponds to the real composition of the azeotrope and to find on the graph how far point F, is shifted to one side or another from the saddle point $(\pm)Az$. The whole procedure may be called the "crossing isobars" method.

The crossing isobars method

In Fig. 1 the concentration triangle is presented with the projection of the top-ridge boiling-temperature isobar $H(\pm)Az[(-)A,P]$. Point $(\pm)Az$ corresponds to the composition of the saddle azeotrope $[(-)A,P(+)H]$, composed of a weak acid, A, a weak base, P, and a hydrocarbon, H.

The experiments should start with the fractional distillation of a suitably chosen ternary mixture of A,P and H. Because of the very flat surface of the tridimensional boiling-temperature isobar, the composition of the main fraction, F, differs somewhat from the composition of the saddle azeotrope $(\pm)Az$. In Fig. 1 such a case is presented. For the sake of clarity, let us examine three different results of the fractional distillation: (1) the coincidence of point $(\pm)Az$ with F; (2) the location of point F on the horizontal line drawn through point $(\pm)Az$; (3) its location somewhere not far from $(\pm)Az$ inside triangle $HP[(-)A,P]$. In all three cases ebulliometric measurements have to be carried out. They consist in four independent measurements, in each of which, at the start, the two- or three-stage [2] ebulliometer should be filled with a new portion of fraction F, and small amounts of mixtures 1, 2, 3 or 4 have to be added several times so as to examine four sections of the boiling temperature isobars, $F1$, $F2$, $F3$ and $F4$.

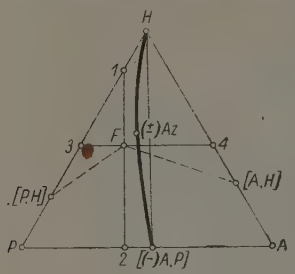


Fig. 1. Schematic presentation of a ternary, positive-negative azeotrope, composed of a weak acid A, a weak base P, and a hydrocarbon H. Points $(\pm)Az$ $[(-)A,P]$ and F correspond, respectively, to the compositions of the saddle and negative azeotropes and of the main fraction collected in the course of the fractional distillation of a suitable mixture of A, P and H. Points 1, 2, 3 and 4 present the compositions of the binary mixtures which are used in four independent ebulliometric measurements for establishing the shapes of four sections of the boiling temperature isobars, $F1$, $F2$, $F3$ and $F4$. Point F does not coincide with point Az

In Fig. 2 *a*, *b* and *c* the shapes of the respective boiling temperature isobars are presented. Scheme *a* corresponds to the case in which the main fraction, F, obtained by fractional distillation coincides exactly with the composition of the ternary saddle azeotrope $(\pm)Az$. Because the saddle point coincides with the minimum on the top-ridge line the two isobars, $F1$ and $F2$, are tangent to the abcissa and their curvature is convex to this axis. As to the sections $F3$ and $F4$, they are also tangent to the horizontal line drawn through F but both of them are concave, as shown in scheme *a*.

Scheme *b* represents another case, that in which the isobar represented by curve $F4$ contains a maximum, which proves that in fraction F, a lack of components is found in the mixture represented by point 4 as compared with the composition of the saddle point $(\pm)Az$.

Finally, in the case represented graphically in Fig. 1, the ebulliometric measurements show that the two isobars, $F1$ and $F4$, are characterized by extrema; i. e., section $F1$ has a minimum and $F4$ a maximum. In Fig. 3 the graphical interpolation of the saddle point $(\pm)Az$ is shown.

Results obtained

The experiments were carried out with a system composed of acetic acid (A), pyridine (P), and normal decane (H). They showed that the

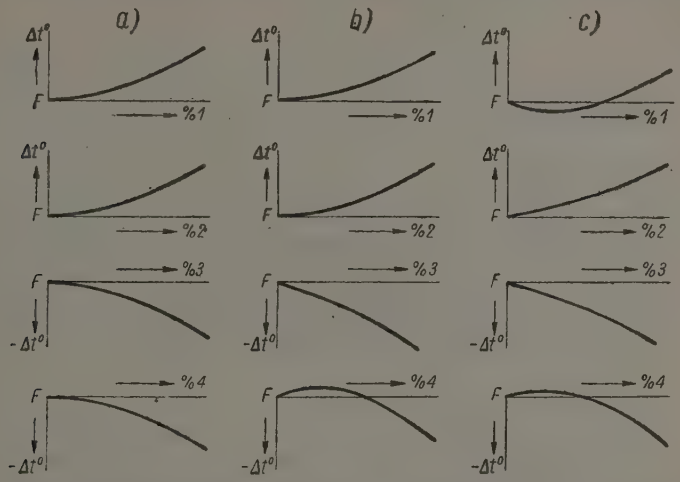


Fig. 2. The three schemes a, b and c correspond to the three respective cases: a — the coincidence of $(\pm)Az$ with F, b — the location of point F on the line $4(\pm)Az$, and c — the location of point F similar to that shown in Fig. 1

composition of the main fraction F was represented by a point lying on the line $4(\pm)Az$ near point $(\pm)Az$. For this reason the shapes of the four isobars were identical with those shown in scheme b (Fig. 2).

In Fig. 4a the graphical interpolation of the point $(\pm)Az$ is shown. The latter is found on the horizontal line $F4$. The composition of the saddle azeotrope is practically identical with that which corresponds to the maximum of the boiling temperature isobar $F4$, as shown in Fig. 4a. Isobar $F4$ is the only one that is characterized by an extremum. The composition of the saddle azeotrope is represented by the point $(\pm)Az$ lying on the line $F4$. (Fig. 4b).

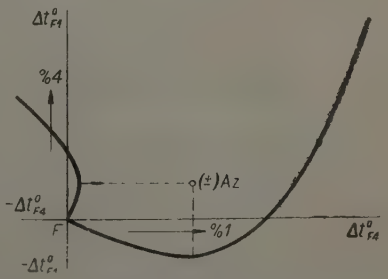
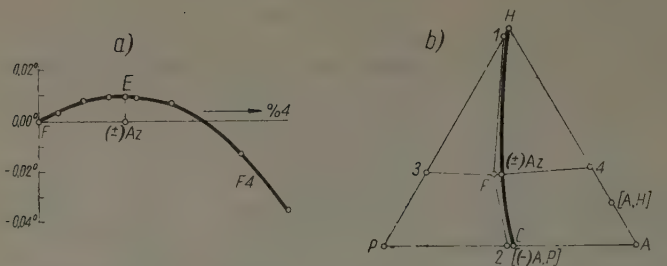


Fig. 3. Graphical interpolation of the location of point $(\pm)Az$

In Table I the boiling temperature differences ($t_F = 0$) for the four ebulliometric measurements are given. From the data obtained we see that only one isobar, $F4$, is characterized by an extremum.



Figures 4a and 4b. Graphical presentation of the case in which only one isobar. $F4$, (see Fig. 2b) is characterized by a maximum. In triangle APH (scheme *b*) is shown the ternary positive-negative azeotrope composed of acetic acid (A), pyridine (P), and normal decane (H). The difference is shown between the composition of the main fraction F and that of the azeotrope under investigation, $(\pm)Az$. 1, 2, 3 and 4 are the binary mixtures used for establishing the four boiling-temperature isobars shown schematically in Fig. 2b

TABLE I

The boiling temperature differences ($t_F = 0$) for the four ebulliometric measurements. Isobar sections for mixtures of F with 1, 2, 3 or 4, respectively

$F1$		$F2$		$F3$		$F4$	
%1	Δt^0	%2	Δt_0	%3	Δt^0	%4	Δt^0
0.90	0.001	1.22	0.000	1.55	−0.010	0.96	0.003
2.02	0.001	2.46	0.001	3.38	−0.029	1.85	0.008
3.28	0.004	3.61	0.002	4.35	−0.037	2.69	0.009
5.11	0.011	4.80	0.003	5.77	−0.052	3.93	0.009
7.07	0.020	6.31	0.005	7.53	−0.082	5.33	0.007
9.46	0.052	7.81	0.007	13.34	−0.253	6.64	−0.012

General remarks concerning the applicability of the crossing isobars method

In this description of the crossing isobars method, line $1F2$ has been accepted as being vertical and $3F4$ as horizontal. It should be pointed out, however, that, as a rule, the point $(\pm)Az$ lies on a higher level than do those representing the composition of the two positive azeotropes (P,H) and (A,H). The boiling temperatures of these azeotropes are sometimes considerably lower than that of the positive-negative azeotrope $t_{(\pm)Az}$. With those kinds of ternary systems, we may obtain better results by examining, instead of isobars $F3$ and $F4$, the two others, namely, those obtained by mixing F with the azeotropes (P,H) and (A,H), respectively as shown by the dotted lines in Fig. 1. By doing this, it is possible to get two curves characterized by more pronounced curvatures

than in the case examined in this paper. This eventuality should be taken into consideration, and sometimes additional ebulliometric measurements have to be carried out in order to establish the shape of the two additional boiling temperature isobars as shown by the dotted lines in Fig. 1.

Summary

1. For a precise determination of the composition and boiling temperature of ternary positive-negative azeotropes a combined distillation and ebulliometric method should be applied.

2. The method of crossing isobars consists in carrying out four independent ebulliometric measurements in order to establish the shapes of the four sections of boiling-temperature isobars. The initial liquid in each of these measurements is the main fraction, F, obtained by fractional distillation of the ternary system of components forming the saddle azeotrope.

3. If the composition of the main fraction, F, corresponds to that of the saddle azeotrope under investigation, the four boiling temperature isobars, obtained by mixing the main fraction, F, each time independently with mixtures 1, 2, 3 or 4, as shown in Fig. 2a, contain no extrema. The extrema appear if the composition of the main fraction, F, is not identical with the point $(\pm)Az$, which corresponds to the real composition of the saddle azeotrope.

4. Two cases of a lack of identity between the composition of fraction F, and point $(\pm)Az$ have been discussed, and the graphical interpolation of point $(\pm)Az$ has been shown on Fig. 2a and b.

5. In the experiments carried out to prove the effectiveness of the crossing isobars method the system used was composed of acetic acid (A), pyridine, (P), and normal decane, (H).

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CHEMISTRY

X-Ray Analysis of Lanthanum Hydrides

by

B. STALIŃSKI

Presented by W. TRZEBIATOWSKI on September 15, 1955

Lanthanum hydrides were prepared in a composition range of from $LaH_{0.10}$ to $LaH_{2.97}$, using an apparatus previously described [1] as well as hydrogen produced by dissociation of titanium hydrides. The lanthanum metal was obtained through electrolysis of a mixture of fused salts ($LaCl_3 + KCl + CaF_2$), and the metal content ($99.7 \pm 0.2\%$) was determined from the volume of hydrogen evolved during the dissolution of the sample in hydrochloric acid.

Lanthanum hydrides containing up to 67 at $-\%$ H, were prepared from c. 0.1 g. metal samples at 300°C., the hydrogen being added in small portions so as to control the violent reaction. The final hydrogen pressure was of the order of 0.01 mm. Hg. The samples were annealed for 100 hours at 300°C.

Samples of higher hydrogen content than 67 at $-\%$ were prepared at lower temperatures. The composition of $LaH_{2.97}$ was obtained with an excess of hydrogen of 700—200 mm. Hg pressure by cooling the sample from 300°C. to room temperature.

The powder diagrams show only one regular, face-centred hydride phase homogeneous in the composition range $LaH_{2.0}$— $LaH_{3.0}$ (Fig. 1).

The hydrogen content of the regular β-form of lanthanum is apparently very small, because

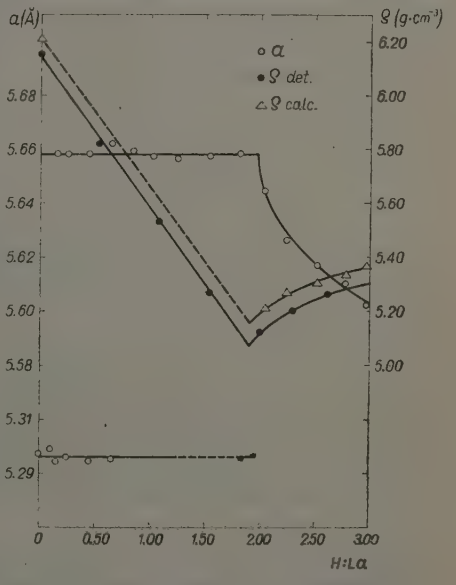

Fig. 1. Lattice constants and densities of the lanthanum-hydrogen system

the lattice dimensions of the metal ($a = 5.29_6$ Å) remain constant through the entire heterogeneous range of the compositions of the metallic and hydride phase, extending to about $LaH_{2.0}$. The hydride phase which occurs already at $LaH_{0.15}$ also possesses, at the above range of compositions, constant lattice dimensions ($a = 5.65_8$ Å). With a higher hydrogen content (ranging from $LaH_{2.0}$ to $LaH_{3.0}$) the lattice constant diminishes and at $LaH_{2.97}$ reaches the value of 5.60_2 Å.

According to the results of Dreyfus-Alain [2], [3], which were obtained through hydrogenation of small lanthanum samples (5 mg.), at least two regular face-centred hydride phases may exist; one occurring at hydrogen pressures of up to 4.1 mm. Hg with $a = 5.65_0 - 5.66_2$ Å, the other existing at higher hydrogen pressures with $a = 5.69_6$ Å. Two further systems of lines were detected by this author and attributed to non-identified structures of lower symmetry.

To prove our experiments, six lanthanum hydride samples, each weighing 2.2 – 3.5 g. were prepared and their densities (ϱ) at 20°C. determined. High boiling ligroin, freshly distilled in the presence of liquid sodium, was used as pycnometric medium.

It was found that the density of lanthanum metal (6.15_5) gradually diminishes with increasing hydrogen content, reaching the (interpolated) value of 5.07 at $LaH_{1.93}$, then increasing to 5.26 at $LaH_{2.63}$.

Figure 1, representing the determined and calculated X-ray densities, shows that these results fully confirm the supposition based on the powder diagrams, namely that under the above-mentioned conditions, only one hydride phase of variable composition exists.

It may be assumed that, of the 12 hydrogen atoms included in the elemental cell, eight are located in tetrahedral holes and four in octahedral interstices. These last seem to be bound differently owing, probably, to the change observed in the lattice dimensions of the hydride phase: these are constant up to the composition $LaH_{2.0}$ and then gradually diminish at higher hydrogen contents ($LaH_{2.0} - LaH_{3.0}$).

Thus, the binary system lanthanum-hydrogen would seem to offer an interesting example of parallelism with transitional phases, changing continuously the fluorite-type structure of LaH_2 into the bismuth fluoride structure of LaH_3.

The author is greatly indebted to Professor W. Trzebiatowski for his interest in the work here presented.

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ERRATA AU VOLUME III

Page/ligne	Au lieu de	Lire
18_9	provided $r<k$—1	provided $r<n$—1
135_6	Fig. 2 Fig. 3	Fig. 3 Fig. 2
136_2	*naturels*	*irrationels*
145_4	*l'hypothèse*	*l'hypothèse Q* et
146_4 147_7 147_8	*l'Hypothèse*	*l'Hypothèse Q* et
149^4	to t. Then	to t and in 1 with respect to x also. Then
186_6	$\mu\left(\frac{\partial u}{\partial x}\right)^2+..$	$\mu\left[\left(\frac{\partial u}{\partial x}\right)^2+...\right.$
205_3	$...=2e^{i0}+$	$...=2e^{-i0}+$
253_9	*indépendant*	*indépendant en dimension m*
253_8	dépend	dépend en dimension m
253_7	indépendants	indépendants en dimension m
253_6	$J(X_0, Y_0)$	$J_m(X_0, Y_0)$
253_5	l'index	l'index $J_m(X_0, Y_0)$, où $n<m<2n$
253_2	polytope	polytope de dimension n, où $n<m<2n$
253_2	$J(X_0, Y_0)$	$J_m(X_0, Y_0)$
311^{11}	u_α	$u_{,\alpha}$
311_{10}	u_n	$u_{,n}$
314^4	$... \int d_{(3)}\bar{\varrho} e^{-\bar{k}_\varrho} V_{np}(\varrho)\psi(\varrho)$	$.... \int d_{(3)}\bar{\varrho} e^{-i\bar{k}_\varrho} V_n p(\varrho)\,\psi(\varrho)$
315^1	$\lambda = \frac{...}{(...)(k_d^3 - k'p + \gamma^2 - i2\gamma k'_p)}$	$= \frac{...}{(...)(k_d^3 - k'p^2 + \gamma^3 - i2\gamma k'p)}$
315^5	$^{end}\operatorname{arctg}\frac{2\gamma k_d}{\gamma' + k'p^2 - k_d^2}$	$^{end}\operatorname{arctg}\frac{2\gamma kd}{\gamma^2 + k'p^2 - k^2 d}$
317_3	$\bar{\alpha}' = 3.08$	$\alpha = 3,08...$
317_4	$\Phi_\alpha(r)$	$\Phi_{\bar{\alpha}}(r)$
318^2	$...(...\bar{k}\bar{r}))$, $n_t = \frac{2e^2 M_t^*}{\hbar^2 k}$	$...(...\bar{k}_t\bar{r}))\, n_t = \frac{2e^2 M_t^*}{\hbar^2 k_t}$

Page/ligne	Au lieu de	Lire
324_2	2943	293
377^9	December 13, 1955	December 13, 1954
410_5	$\frac{\Phi(x)}{\|\Phi_\varepsilon(x)\|}$	$\frac{\Phi_\varepsilon(x)}{\|\Phi_\varepsilon(x)\|}$
469^1	Die Bedingung (B) ist immer erfüllt, wenn H bikompakt ist.	Die Bedingung (B) ist bei geeigneter Wahl der invarianten Metrik immer erfüllt, wenn die Untergruppe H bikompakt ist
485^8	1936 e	1906 e
485^{11}	151	1951
495^{10}	Trichloromethylnitromethane [4]	Trichloromethylnitromethane [9]

Ajouter

P. 17: Add at the end of the paper *On the equation* $x_1 x_2 \dots x_n = t^k$, the following footnote: The Theorem may be deduced from theorem (4), (2) of the paper of: "*A type of multiplicative diophantine system*", Am. J. of. Math. **55** (1953), by putting $k=n=1$. It is to be noticed that the proofs of those theorems are different.

P. 129 in fine: I am indebted to prof. Jarnik, for the information that M. Kössler discovered already in 1929, *Dvé poznámky k theorii ciselné,* Čas. pro pēst. mat. a fys. **58** (1929) 30—36 the formulae (1), (2) and the formulae for the series $\sum_p \frac{1}{p^s}$ of my paper *On powers,* Bull. Acad. Polon. Sci., Cl. III, **3** (1955) 129—132. My proofs, however, differ from those of Kössler.

P. 145_{7-8}. HYPOTHÈSE *Q. Chaque point* $P \in B$ *appartient à un voisinage* $V (V \subset B)$ *constituant une image homéomorphe d'une boule euclidienne à n dimensions.*